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SPECIFIC HEAT OF LAC

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ABSTRACT. Specific heats of different varieties of lac and lac constituents have been determined with a vacuum calorimeter which in principle is the same as was employed by Nernst and Lindemann for poor heat-conductors. The constructional details of the calorimeter have been described in the paper The first series of experiments show that the specific heat of shellac practically remains constant over the temperature range of 10°C to 40°C and the value obtained is between 0·36 and 0·38 cals./gm./°C. Higher and higher values are obtained as determinations are made at higher and higher temperatures. Seedlac, in general, has a slightly higher value of specific heat than shellac owing probably to the presence of slightly higher percentage of water. Heat-hardened lac has been found to give a lower value of specific heat due to the elimination of water during the hardening process. It has been noticed that lac begins to absorb heat of fusion even at so low a temperature as 40°C which is ordinarily believed to be far away from its softening range of temperature.

INTRODUCTION

An elaborate study has been made on the thermal properties of most of the synthetic resins, but since lac is a natural resin and as such it cannot be a very standardised product, adequate attention was not paid to a careful study of its thermal properties so far. Some data on its thermal conductivity,[1] thermal expansion,[2] softening and melting points[3] and fluidity[4] are available. But no record of the specific heat of lac is available till now. Verman[5] pointed out that the study of this property at different temperatures might be useful in obtaining an idea of the change which lac undergoes on heating.

The problem of storing lac for a long period without having its thermal and electrical properties appreciably altered is engaging the attention of shellac-manufacturers. Cold storage of lac is being considered by some as a probable solution. Data on the specific heat of lac will be very useful for this purpose.

The object of the investigation was to supply specific heat data sufficiently accurate for ordinary purposes but not such as would have necessitated extreme precautions and very elaborate arrangements. This was in order to simplify unnecessary complications considering the nature of purity that we can ordinarily expect from a sample of shellac. Though, therefore, a vacuum calorimeter was finally used in these investigations, the use of a calibrated thermo-couple for the measurement of temperature or of potentiometric evaluation of voltage and current that is usually associated with such a calorimeter has been purposely omitted.

It should be clearly understood, however, that for substances, like resins, which have a softening range of temperature but no definite melting point, the determination of specific heat could be done only at temperatures tolerably removed from the softening range as otherwise latent-heat factors would vitiate the results.

EXPERIMENTAL

Preliminary Experiments

Ordinary calorimetric method was first used for the determination of specific heat of lac, the calorimeter being a well-insulated double-walled one and paraffin oil the calorimetric liquid. Lac in the form of powder was enclosed in a small flat copper container and was never heated above 45°C in order to keep it far below its softening point. Determination was made within two ranges of temperature, *viz.*, between room temperature and 45°C and between room temperature and 0°C. For the higher range of temperature samples were heated having been suspended inside a wide tube surrounded by a jacket through which hot water at some definite temperature could be circulated. For the lower range of temperature, however, the jacket could be filled with crushed melting ice and a small cruicible containing fused calcium chloride was placed on the bottom cork closing the inner tube in order to absorb moisture from the enclosed air. Determination of specific heat was made in the usual way by noting the rise or fall of temperature of paraffiin oil and applying proper corrections.

The values obtained in this way for a few samples of shellac were near about 0·5 cals./gm./°C within the higher range of temperature and about 0·3 to 0·4 for the lower range. As this difference was large, the use of a more accurate method of determining specific heat at different temperatures was considered necessary in order to ascertain to what extent the effect of temperature was responsible for it.

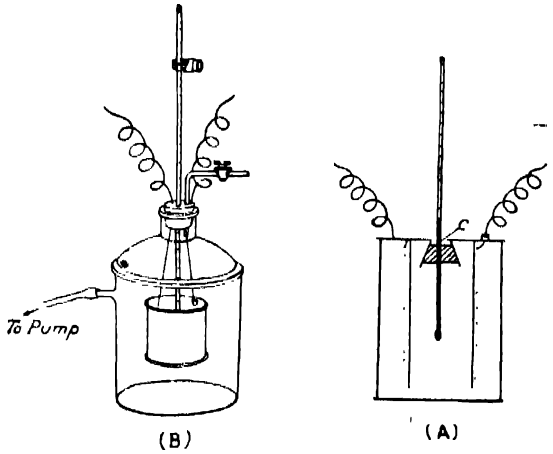

FIGURE 1
Vacuum Calorimeter

For this purpose a vacuum calorimeter, which was essentially the same as used by Nernst and Lindemann [6] for the determination of specific heat of poor heat conductors at low temperatures, was employed. The diagrammatic sketch of the design has been shown in Figure 1(A). The outer cylindrical can having a length of 9·5 cms. and a diameter of 3·5 cms. was made of thin sheet copper and the inner tube, which was fixed on the top cover coaxially with the outer cylinder, was also made of the same material having a diameter of exactly half of the outer one. A heating coil of S.W.G. No. 36 constantan wire having a resistance of 5·70 ohms was wound on the inner tube using a thin mica sheet as insulation. One terminal of the coil was soldered to the body of the calorimeter, while the other was brought out through a small hole on the cover having been properly insulated by varnished cotton sleeve and sealed in some insulating cement. A long thermometer, graduated to tenths of a degree and which could easily be read to an accuracy of 1/20th of a degree by clamping a reading lens on it, was fixed along the axis of the cylinders through a rubber cork fitted on a conical hole on the top as shown at C in the figure. A thin layer of paraffin was applied on the cork to make the lid vacuum-tight. The bottom lid could be unsoldered for the purpose of filling the calorimeter. The capacity of the vessel was about 65 c.c. The calorimeter was placed inside a small Witt's filtering vessel, the thermometer projecting outside. The vessel could be evacuated to a low vacuum in order to reduce as much as possible loss or gain of heat from the calorimeter to its surroundings by gaseous conduction or convection. The whole assemblage could be placed inside a big thermostat whose temperature could be kept constant to within 0·1°C throughout the range of investigation.

Method of Determination

The procedure was to fill the calorimeter with the substance in the form of powder and solder the bottom lid so as to make it vacuum-tight. A thin coating of collodion was sometimes applied on the soldered portion for this purpose. The assemblage was then put in the thermostat to attain its temperature. When the thermometer in the calorimeter registered the temperature of the thermostat, the space surrounding the calorimeter was evacuated to a low vacuum. A low current was then passed from a 4-volt lead storage battery of large capacity through the heating coil for some definite time and the temperature noted at the end of every minute during heating and every half minute after that for the purpose of applying radiation corrections.

Calibration

The calorimeter was very carefully calibrated with Schering's pure aluminium metal powder and subsequently its heat capacity thus obtained used in the

determination of specific heat of copper dust and graphite powder. The results obtained agreed to within 5% of their values given in the International Critical Tables.[7] Pure Naphthalene was also used as it had been employed by many previous workers[8] for the calibration of a vacuum calorimeter, and as it is also a poor conductor of heat like shellac. The result was satisfactory and was accurate within the limits of error stated above. The heat capacity of the calorimeter was 14·3 calories/°C.

RESULTS

For a few samples of lac the time of heating was 15 minutes for the first series of experiments and the rise of temperature about 4°C. The heating current was kept constant at 0·35 ampere throughout the experiment. The results of such determinations have been shown in Table I. It will be seen from the table that lac generally begins to absorb heat of fusion from about 40°C and therefore

TABLE I

Sample	Wt taken in gms	Range of temperature in degrees centigrade	Sp. ht. in cals./gm./°C.	Sample	Wt. taken in gms.	Range of temperature in degrees centigrade	Sp ht in cals./gm./°C.
Kusum shellac	60·3	10—15	0·37	Heat-hardened shellac.	58·3	10—15	0·33
		15—20	0·37			15—20	0·33
		20—25	0·37			20—25	0·34
		25—30	0·37			25—30	0·33
		30—35	0·38			30—35	0·34
		35—40	0·38			35—40	0·35
		40—45	0·44			40—45	0·34
		45—50	0·56			45—50	0·36
Palas shellac	59·5	10—15	0·35	Chemically hardened shellac (shellac exposed to HCl vapour).	55·2	10—15	0·36
		15—20	0·36			15—20	0·36
		20—25	0·36			20—25	0·35
		25—30	0·36			25—30	0·36
		30—35	0·35			30—35	0·36
		35—40	0·37			35—40	0·37
		40—45	0·42			40—45	0·39
		45—50	0·55			45—50	0·43

the apparent specific heat is high at higher temperatures. As a result of this finding specific heat was determined for a number of samples between the range 10°C and 30°C. The time of heating was between 1 hr. and 1½ hrs. for different samples for this range of temperature. Table II shows these results. The input energy could be measured within an accuracy of 1% and the temperature within 1½%. Taking into consideration the accuracy of radiation corrections, the results are not generally claimed to be more accurate than within 5%. In the worst cases, the error may be slightly more. For ordinary purposes, however, this accuracy is considered sufficient.

TABLE II

Sample	Range of temperature 10°C—30°C		Sample	Range of temperature 10°C—30°C	
	Wt. taken in gms.	Sp. ht. in cals./gm/°C.		Wt. taken in gms.	Sp. ht. in cals./gm/°C.
Kusum shellac	60·3	0·37	Pure lac resin (extracted by A-U method)[9].	57·8	0·34
Kusum seedlac	58·8	0·40			
Palas shellac	59·5	0·36	Soft resin (Ether-soluble).	102·4	0·48
Palas seedlac	61·1	0·40	Shellac wax	76·5	0·43
Khair shellac	59·2	0·37	Heat-hardened shellac.	58·2	0·34
Khair seedlac	60·8	0·41			
Pure lac resin (Ether-insoluble).	58·2	0·34	Heat-hardened pure lac resin.	54·6	0·32
			Chemically hardened shellac.	55·2	0·36

DISCUSSION

Comparing the values of specific heat for some other plastics [10] it is found that shellac has almost an identical value. For example, 'Pyroxylin' (Nitro-cellulose plastic) gives for its specific heat 0·34 to 0·38, phenol resins give 0·33 to 0·37, gutta-percha and balata 0·402 and vulcanised-rubber 0·415. For shellac wax, however, the value obtained is definitely lower than that for paraffin wax (mineral wax, sp. ht. 0·69) between the same range of temperature and even slightly lower than that for beeswax (animal wax, sp. ht. 0·477) between 20°C and 30°C.

It will be seen that the values of specific heat of heat-hardened shellac and heat-hardened pure lac resin are lower than those of ordinary shellac and pure

lac resin. This may be explained by supposing that during the process of hardening by heat both shellac and pure lac resin lose some amount of water and form into a condensation product.[11, 12] So naturally the amount of heat required to raise its temperature through one degree may be expected to be less according to Kopp-Neumann law as the specific heat of water is sufficiently high. This explanation gains further support from the fact that the specific heat of chemically hardened shellac is not so low, as there the hardening process is considered to be one of polymerisation without elimination of water.[13]

To calculate the amount of water that is lost by heat-hardening, one of the pure lac resin samples of which the specific heat was determined first, was heated at about 120°C for 15 hours and the specific heat was then determined again. It was found that the value of specific heat fell from 0·34 to 0·32. A sample of Kusum shellac similarly showed a reduction of specific heat, from 0·37 to 0·34. But, as the difference in specific heat was of the same order as the possible experimental error, no definite conclusions could be drawn from the calculations following Kopp-Neumann law.

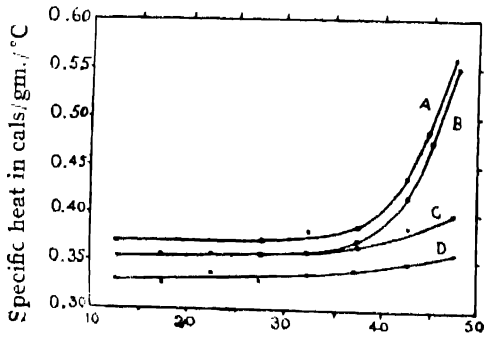

FIGURE 2

Specific heat of lac at different temperatures —
A—Kusum Shellac
B—Palas Shellac
C—Chemically hardened shellac
D—Heat-hardened shellac

It is evident from Table I that the specific heat of lac samples does not show much variation between the temperatures 10°C and 35°C but higher and higher values are obtained as determinations are made at higher and higher temperatures. Figure 2 shows this variation. This simply means that lac begins to absorb a small amount of heat even at so low a temperature as 40°C though this temperature is far removed from its ordinarily believed 'softening range' (56°-75°C).[14] The study of the variation of refractive index of lac with temperature[15] also

revealed similar changes near about the same temperature. On a study of the coefficient of cubical thermal expansion of shellac determined at different temperatures over the range −80°C to 200°C, Samsoen [2] found out a transition temperature at about 46°C. The expansion-coefficient above 46°C was about four times the value below it. He also found out such characteristic temperatures in the case of many other amorphous substances such as, glass, tar, rosin, etc., and has shown that other physical properties of these substances also undergo a sudden change near about their respective transition temperature. Such temperatures have been observed for many other substances by other workers [16] also. These specific-heat experiments, however, confirm Samsoen's observation regarding the transition temperature of shellac near about 46°C. Apparent higher values of specific heat at increased temperatures, therefore, indicate merely the influence of latent heat. In other words, when lac is heated physical changes begin to take place long before they are detected by the standard methods [17] for the determination of softening points. The softening point as determined by these methods, therefore, denotes a definite stage during the softening process, but it does not really indicate the starting of it. The large difference obtained for the specific-heat values between the two temperature ranges in the preliminary investigations was therefore the result of slight softening at the higher range of temperature. Tamman's [3] observation that shellac loses its brittleness at about 30°·5C and the softening range is between 30°·5C and 56°·5C is supported by these experiments.

The slightly higher values of specific heat in the case of seedlac than for sheliac may be accounted for by the presence of slightly higher percentage of water and by the absence of any heat treatment during manufacture. The apparent change of specific heat with temperature in the case of hardened lac has been found to be small, as might be expected since their softening points are high. The specific heat of shellac is intermediate between those of soft resin and pure lac resin and it agrees well with the calculated value considering lac as composed of about 75% pure lac and 25% soft lac.

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